Chapter 6

Data Quality

The data quality indicators for CASTNet include precision, accuracy, completeness, representativeness, and comparability. Information on precision, accuracy, and completeness are presented to illustrate the overall quality of CASTNet measurements and to demonstrate that the measurement processes collect and generate data of the high quality required to meet project objectives.

The CASTNet program was designed to fulfill the following objectives: 1) monitoring the status and trends in air quality and atmospheric deposition; 2) providing atmospheric data on the dry deposition component of total acid deposition, rural ground-level ozone, and other forms of atmospheric pollution that enter the environment as particles and gases; and 3) assessing and reporting geographic patterns and long-term, temporal trends in ambient air pollution and acid deposition. Data quality indicators (DQI) have been formulated to gauge the achievement of these CASTNet objectives. DQI are the quantitative and qualitative descriptors used in interpreting the degree of acceptability and utility of the data collected. The DQI for CASTNet include precision, accuracy, completeness, representativeness, and comparability. In the following sections, results for field precision, laboratory precision and accuracy, and completeness of direct measurements for 2000 have been presented along with historical statistics to provide an overall indication of data quality over the history of the network. CASTNet DQI are discussed in detail in the CASTNet QAPP (Harding ESE, 2001b).

Precision

DQI, in terms of precision and accuracy of filter pack concentration data, are listed in Table 6-1. The precision criteria apply to pairs of concentration data collected at collocated sampling systems and also to laboratory in-run replicate data. During 2000, collocated sampling systems were operated at Ashland, ME (ASH135/235) and Mackville, KY (MCK131/231). Over the history of the network, collocated systems have been operated at ten sites. In Figure 6-1, bar charts present precision statistics in terms of mean absolute relative percent difference (MARPD) for both the historical

Figure 6-1. Historical and 2000 Precision Data
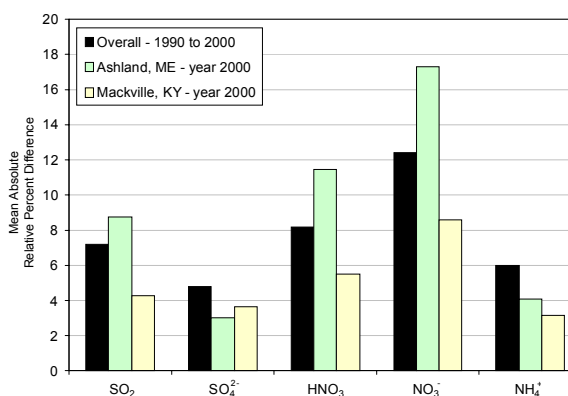
database and the 2000 data for ASH135/235 and MCK131/231. The historical results vary from about 5 percent for SO_4^{2-} to about 12 percent for particulate NO_3^-. The MARPD statistics for SO_4^{2-} and NH_4^+ met the DQI listed in Table 6-1. The results for SO_2 (as SO_4^{2-}) and HNO_3 (as NO_3^-) were above the 5 percent criterion, and the results for NO_3^- were significantly above the 5 percent goal. Precision results for three of the analytes measured at ASH135/235 in 2000 were above the historical results and two were below. All of the 2000 results from MCK131/231 were below the historical results. The precision of the particulate NO_3^- measurements has been consistently worse than the other analytes, possibly because nitrate concentrations are the lowest of all the pollutants. During 2000, NO_3^-

concentrations at Ashland were lower than those typically measured at other sites.

The analytical precision results for 2000 are presented in Figures 6-2 and 6-3. These results were based on the in-run replicates that were analyzed for all three analytes and the three filter types. Five percent of the samples in each batch were randomly selected for replication and the results were compared to the original concentrations. The laboratory precision data met the DQI (Table 6-1).

> *Historical precision results were based on collocated samples at ten sites and laboratory in-run replicate data.*
> - *Precision varies between 5 and 12 percent.*
> - *Precision statistics for SO_4^{2-} and NH_4^+ met the DQI.*
> - *Laboratory precision met all DQI objectives.*

Table 6-1. Data Quality Indicators for CASTNet Laboratory Measurements*

| Analyte	Medium	Method	Precision (MARPD)**	Accuracy (%)	Nominal Detection Limits
Ammonium (NH_4^+)	F	Automated colorimetry	10	90 - 110	0.02 mg-N/L
Sodium (Na^+)	F	ICAP-AE	10	90 - 110	0.005 mg/L
Potassium (K^+)	F	ICAP-AE	10	90 - 110	0.005 mg/L
Magnesium (Mg^{2+})	F	ICAP-AE	10	90 - 110	0.003 mg/L
Calcium (Ca^{2+})	F	ICAP-AE	10	90 - 110	0.003 mg/L
Nitrate (NO_3^-)	F	Ion chromatography	5	95 - 105	0.008 mg-N/L
Sulfate (SO_4^{2-})	F	Ion chromatography	5	95 - 105	0.04 mg/L
Elemental Carbon	QF	TOA	10	90 - 110	$0.10 \, \mu g \text{ -C/m}^3$
Organic Carbon	QF	TOA	10	90 - 110	$0.10 \, \mu g \text{ -C/m}^3$
Total Carbon	QF	TOA	10	90 - 110	$0.20 \, \mu g \text{ -C/m}^3$
Mass	TF	Gravimetric	$\pm 10 \, \mu g$	$\pm 3 \, \mu g$	$2.13 \, \mu g \text{ /m}^3$
Trace/Crustal Elements	TF	XRF	20	90 - 110	$0.001\text{-}0.10 \text{ ng/m}^3$

Note:

C	=	carbon
F	=	filter pack samples
ICAP-AE	=	inductively coupled argon plasma-atomic emission.
MARPD	=	mean absolute relative percent difference
N	=	nitrogen
QF	=	quartz filter
TF	=	Teflo® filter (Harding ESE, 2001b).
TOA	=	thermal-optical analysis
XRF	=	X-ray fluorescence

* The precision criteria apply to the laboratory analysis of field samples and laboratory replicates.
** This column lists precision goals for both network precision calculated from collocated filter samples and laboratory precision based on replicate samples.

For more information on analytical methods and associated precision and accuracy criteria, see the CASTNet Quality Assurance Project Plan (Harding ESE, 20001b).

Figure 6-2. Laboratory Precision Data for 2000
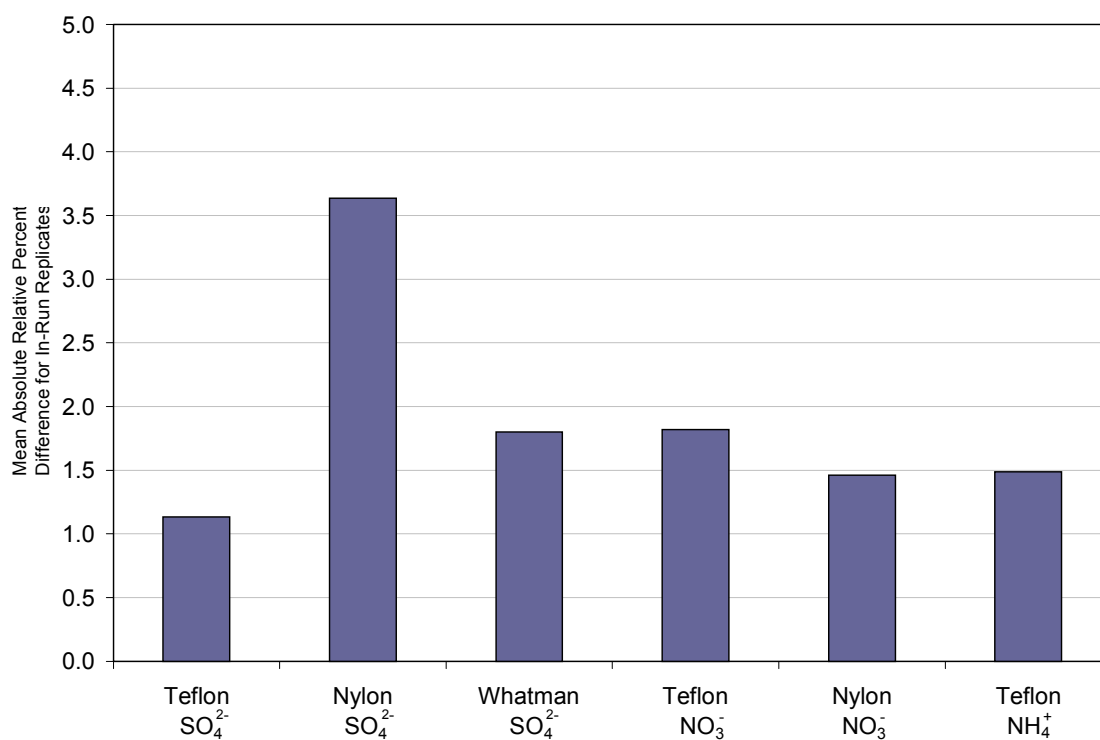
Figure 6-3. Scattergram of Replicate versus Original Values for 2000

$y = 1.0031x + 0.0018$
$R^2 = 0.9999$
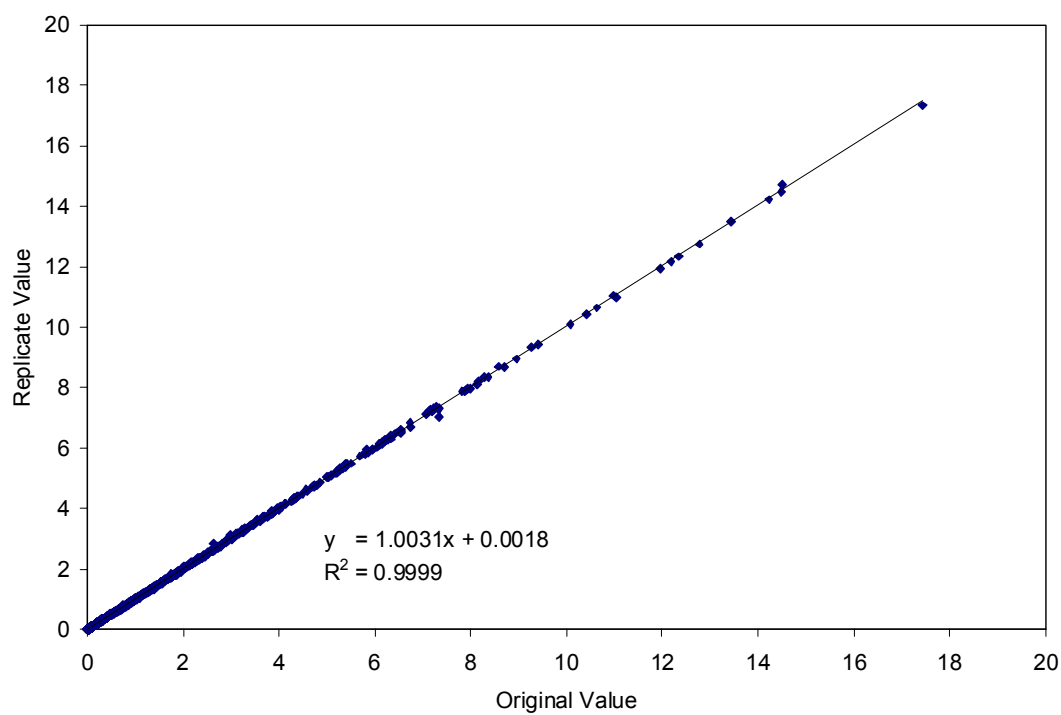
Accuracy

Analytical accuracy was based on the analysis of reference samples and CVS, both of which are traceable to NIST. DQI were met for all analytes and filter types in 2000.

Accuracy of laboratory measurements was assessed through the analysis of reference samples and continuing verification samples (CVS). CASTNet DQI are 5 percent for sulfate and nitrate and 10 percent for ammonium and cations (Table 6-1). Reference samples were procured from an independent laboratory supplier to simulate typical concentrations of the dry deposition filter pack samples. Reference samples, which were traceable to NIST, were analyzed at the beginning and end of each analytical batch to verify the accuracy and stability of the calibration curve. Figure 6-4 presents the percent recovery relative to the target reference values. All analytes and filter types for 2000 met the DQI.

Accuracy was also assessed through the analysis of CVS that were procured from a second independent laboratory. The target value of the CVS solution was NIST traceable and was set to the midrange of the calibration curve. The CVS in 2000 were analyzed every tenth sample to verify no drift in the calibration curve. Figure 6-5 presents the percent recovery of CVS relative to the target concentrations. The DQI were met for all analytes and all filter types.

Completeness

- *Measured parameters routinely met the 90 percent completeness goal for the network.*
- *Completeness for V_d ranged between 85 to 90 percent. Completeness for V_d is generally lower because it depends on the simultaneous completeness for several parameters.*
- *All meteorological measurements exceeded 90 percent completeness for 2000.*
- *All filter and aerosol concentrations measurements exceeded 90 percent completeness for 2000.*
- *Hourly flux values achieved approximately 85 percent completeness in 2000.*

Completeness

Completeness is defined as the percentage of valid data points relative to total possible data points. The CASTNet DQI require a minimum completeness of 90 percent for every measurement for each quarter. In addition, data aggregation procedures discussed in Chapter 1 require approximately 70 percent data completeness for hourly fluxes and weekly concentrations/fluxes in order to calculate weekly and quarterly values, respectively.

Figure 6-6 presents historical percent completeness data aggregated over all sites for continuous measurements, filter pack (dry deposition) concentrations, visibility aerosol concentrations, and hourly dry deposition (flux). This figure does not include data from the fourth quarter 1995 through the second quarter 1996 as this was the temporary shutdown period for most of the sites in the network. The three types of direct measurements generally met the 90 percent completeness goal with the one exception of the aerosol concentrations in 1995. During that year, the schedule for aerosol sampling varied from a range of every three days to every 12 days, before a permanent schedule of sampling every six days was established. Several filters collected during the period of high frequency sampling were deliberately not analyzed resulting in low data completeness statistics.

The bottom graph in Figure 6-6 depicts the completeness of hourly dry deposition fluxes. The MLM was used to calculate V_d in order to calculate fluxes from the modeled V_d and measured concentrations. The completeness of the hourly flux data is dependent on the combined completeness results for several parameters. Hourly V_d values are modeled using several meteorological measurements (e.g., wind speed, sigma theta, solar radiation, temperature, relative humidity, and surface wetness), all of which have a 90 percent completeness requirement. Calculation of modeled hourly V_d values using the MLM also requires estimates of hourly LAI. In other words, one missing meteorological parameter or LAI value invalidates a V_d value. Despite this stringent requirement, the completeness for V_d has been above 85 percent for every year since 1991, which is quite reasonable.

Another way to illustrate completeness is to plot the number of quarters per parameter per year for each of the sites with specific measurements of less than 90 percent. The maximum

number of site-quarters per year equals the number of sampling stations operating during that year multiplied times four. Figure 6-7 shows the number of site-quarters with data completeness of less than 90 percent by year for three continuous measurements: filter pack flow, ozone, and scalar wind speed. The data points in this figure were based on EPA sponsored sites only. Figure 6-7 demonstrates that flow measurements were very stable, with only a few site-quarters per year with less than 90 percent data completeness values. The results from the network for ozone and wind speed show completeness values below 90 percent for only about nine site-quarters per year for the last five years.

Completeness statistics for measurements taken in 2000 have also been compiled. Figure 6-8 shows the completeness data for the CASTNet continuous measurements. Completeness results range from approximately 92 percent for relative humidity to 98 percent for flow. Results for dry deposition filters are shown in Figure 6-9. Completeness exceeded 97 percent for all parameters and all filter types. Results for 2000 for the visibility/aerosol filters are shown in Figure 6-10. The three bars represent $PM_{2.5}$ mass from the Teflo® filters, SO_4^{2-} and NO_3^- concentrations from the nylon filters, and organic carbon levels from the quartz filters. Completeness exceeded 93 percent for the three filter types. As shown in Figure 6-11, completeness results for hourly flux values were approximately 85 percent during 2000.

Summary

The 2000 results for analytical precision and accuracy, and also for completeness data of direct measurements, met DQI. These results illustrate the overall quality of CASTNet measurements. The collocated filter pack precision results, which are directly linked to the quality of field, laboratory, and supporting measurement processes, were quite reasonable. In addition, completeness results of the modeled hourly V_d were reasonable. Historically, the precision statistics for SO_4^{2-} and NH_4^+ have met the DQI. The results for SO_2 and HNO_3 have been above the 5 percent DQI goal, but are considered reasonable. The MARPD data for NO_3^- have been significantly above the 5 percent goal. The results for 2000 are consistent with the historical results and also indicate greater imprecision for lower concentrations (Harding ESE, 2001b). Perhaps, evaluation and possible reformulation of the precision DQI in terms of concentration magnitude and analyte should be considered.

Figure 6-4. Laboratory Accuracy Data for 2000 (Percent Recovery of Reference Samples) (Page 1 of 2)
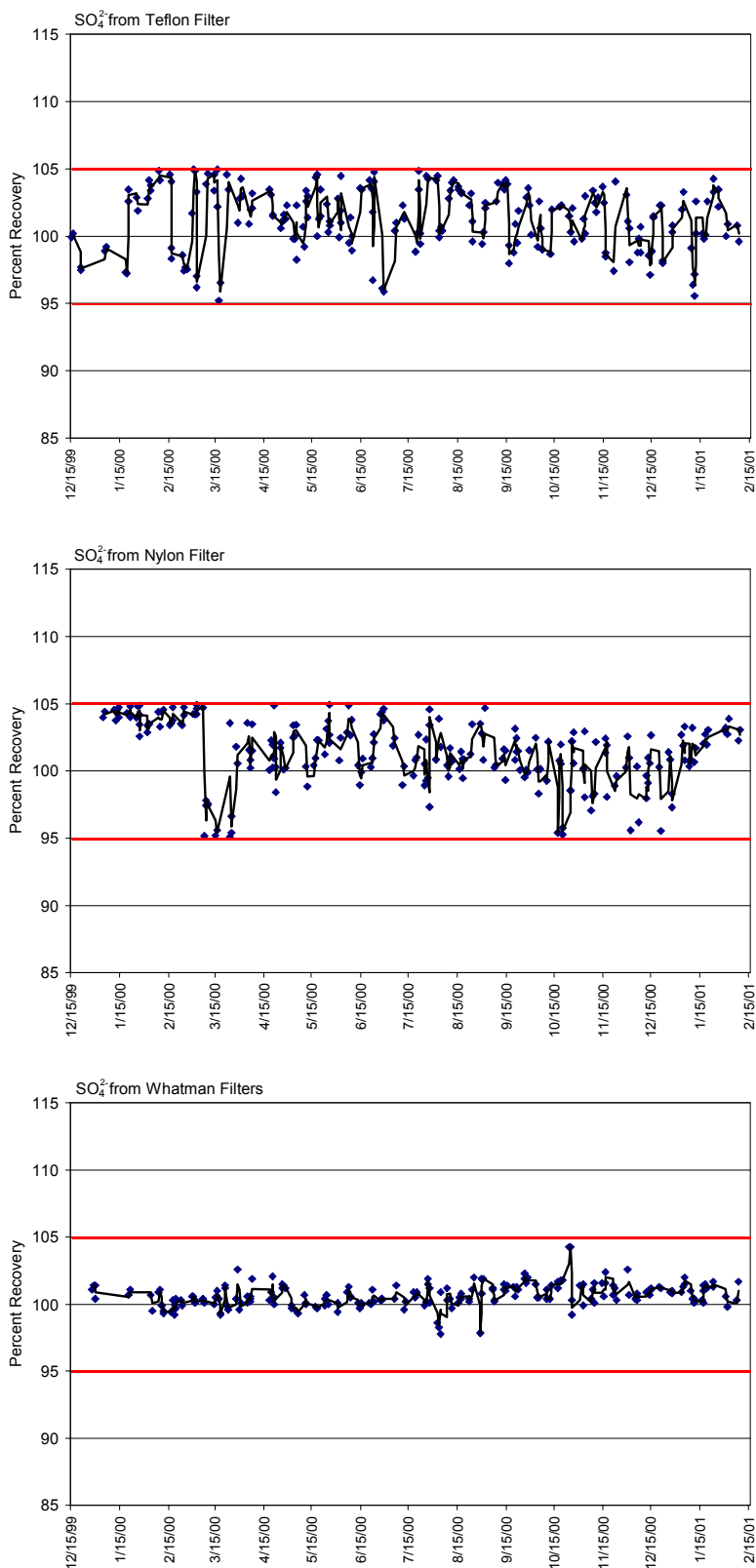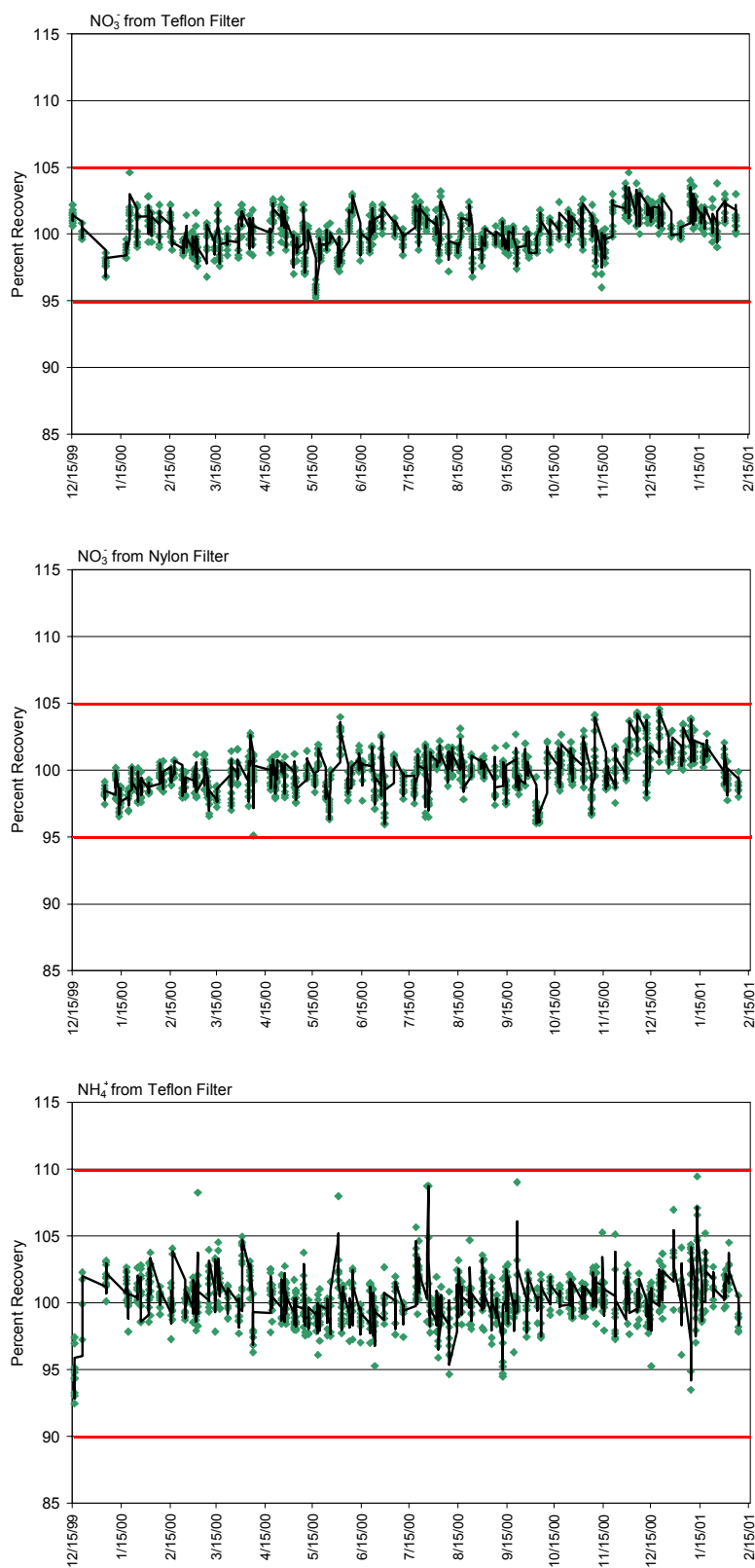

Note: The solid line was fit through the data points using a moving average with a period of two.

Figure 6-4. Laboratory Accuracy Data for 2000 (Percent Recovery of Reference Samples) (Page 2 of 2)
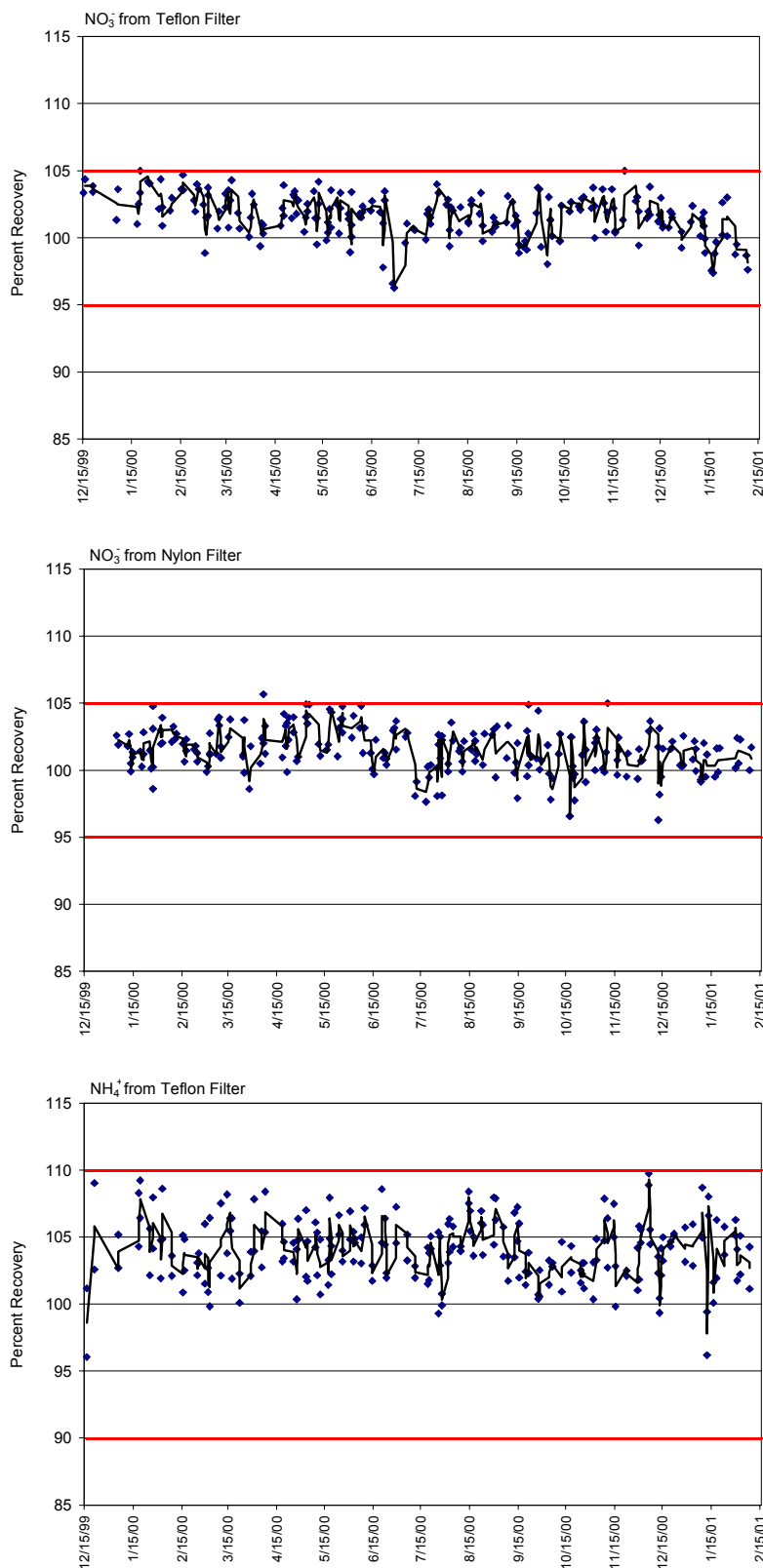

Note: The solid line was fit through the data points using a moving average with a period of two.

Figure 6-5. Laboratory Accuracy Data for 2000 (Percent Recovery of CVS) (Page 1 of 2)
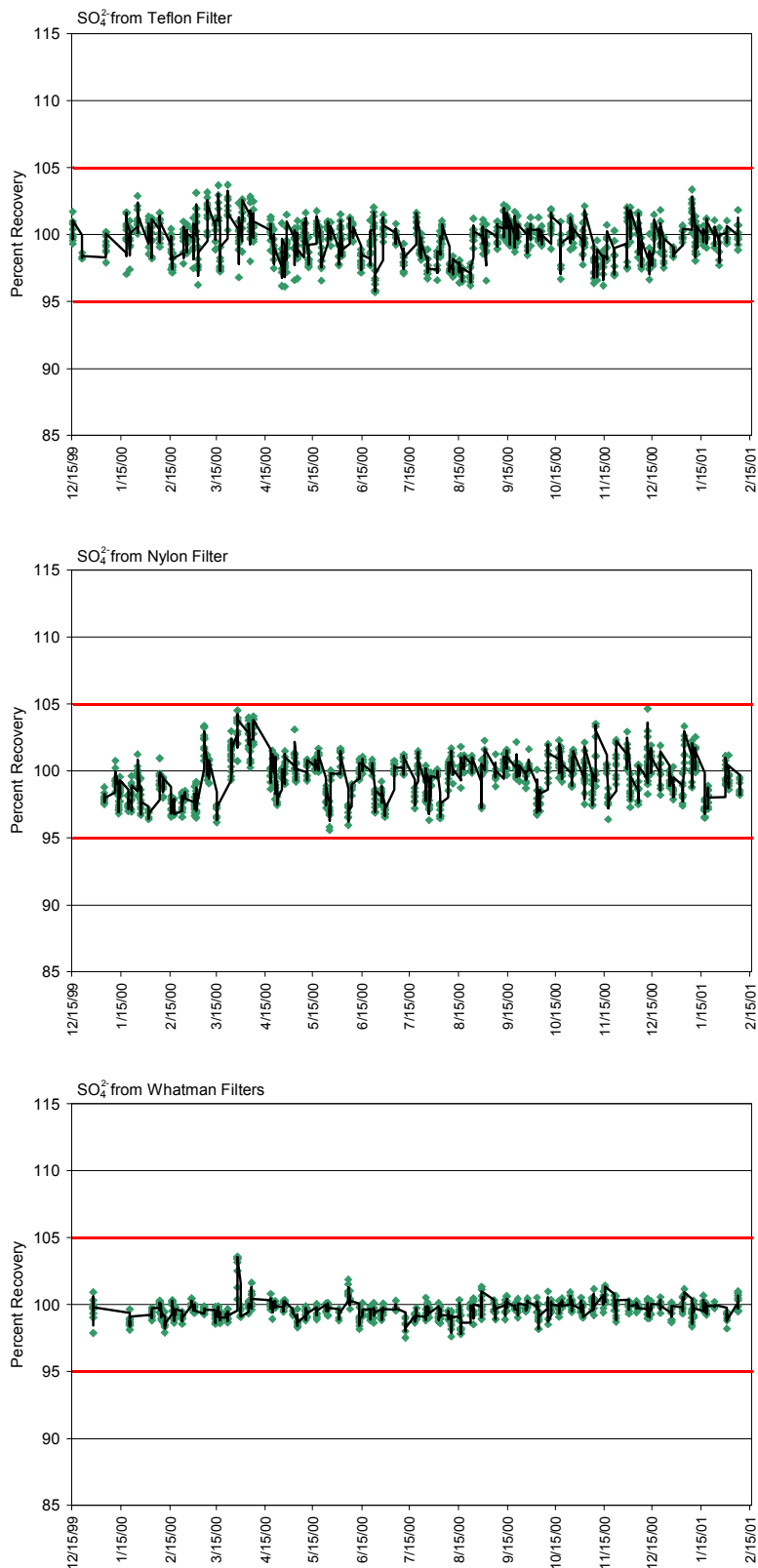

Note: The solid line was fit through the data points using a moving average with a period of two.

Figure 6-5. Laboratory Accuracy Data for 2000 (Percent Recovery of CVS) (Page 2 of 2)

Note: The solid line was fit through the data points using a moving average with a period of two.

Figure 6-6. Historical Percent Completeness*
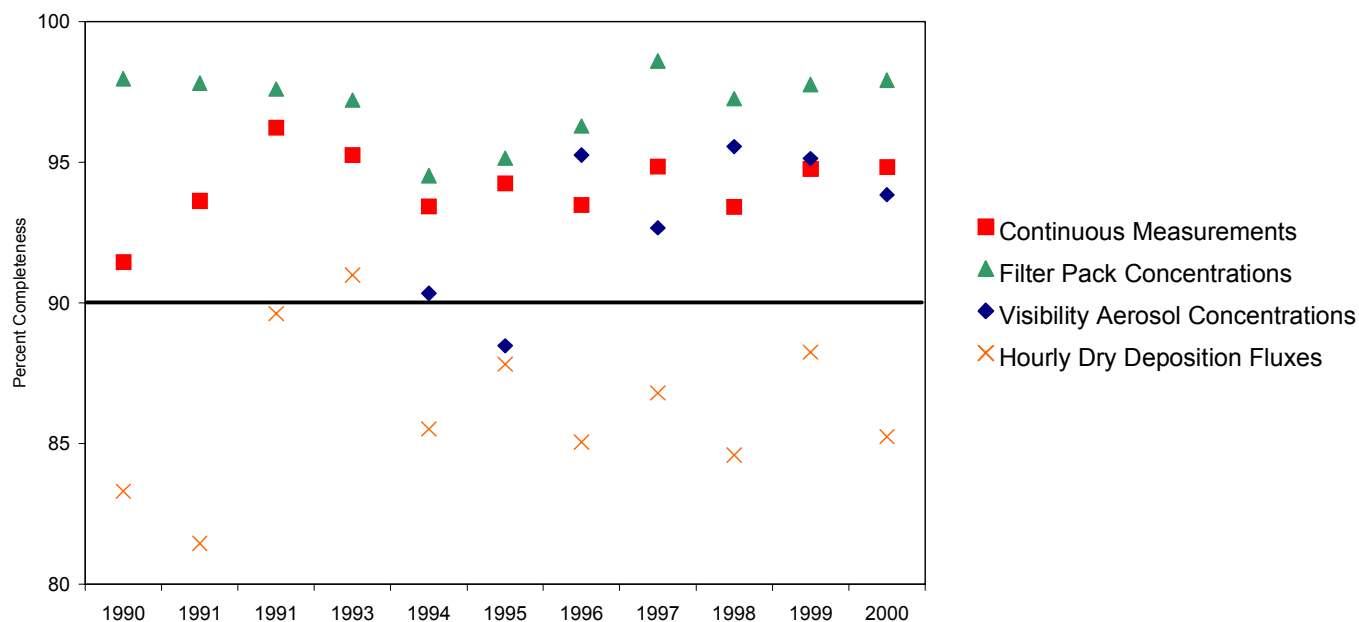
*Completeness goal for CASTNet measurements is 90 percent.

Figure 6-7. Number of Site-Quarters with Data Completeness Less Than 90 Percent for Selected Measurements (1990 through 2000)
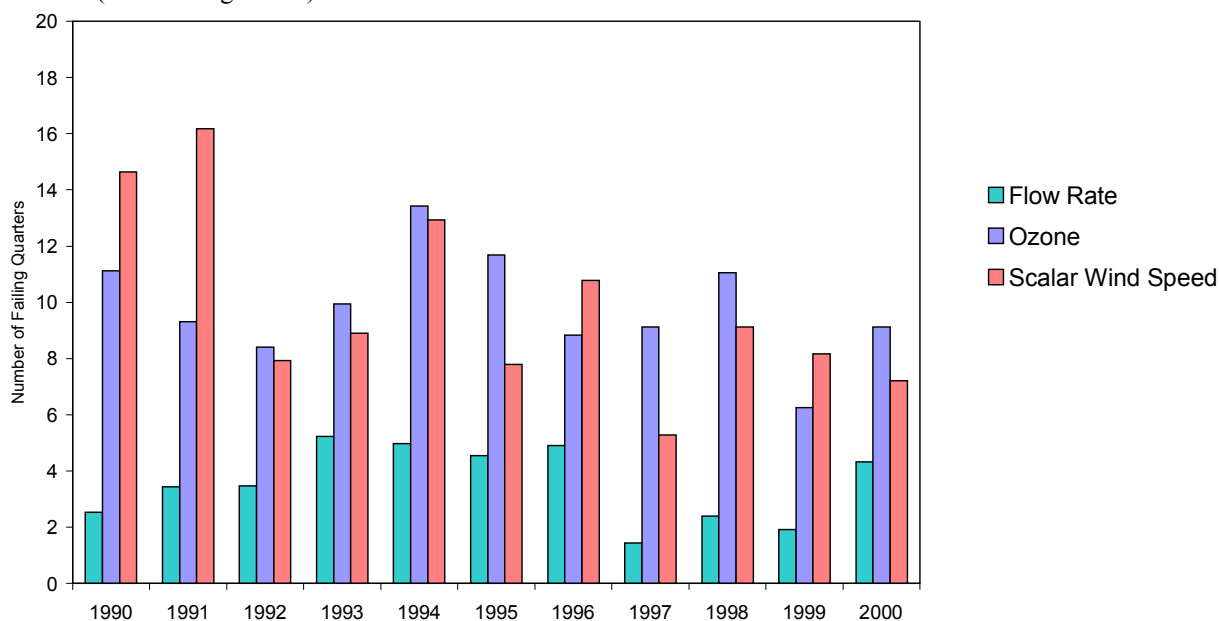
Note: The maximum number of site-quarters per year for each parameter equals the number of sampling stations operating during that year multiplied times four.
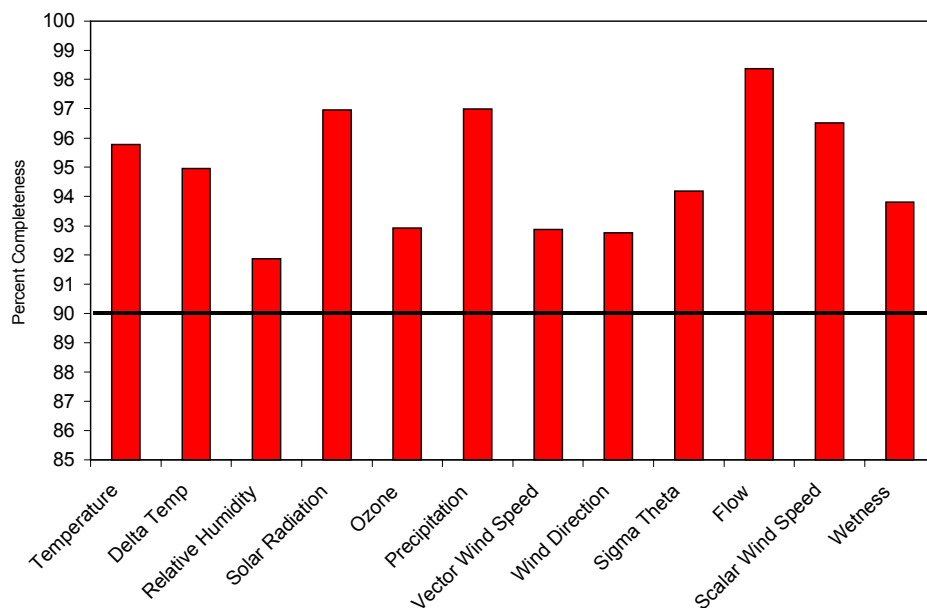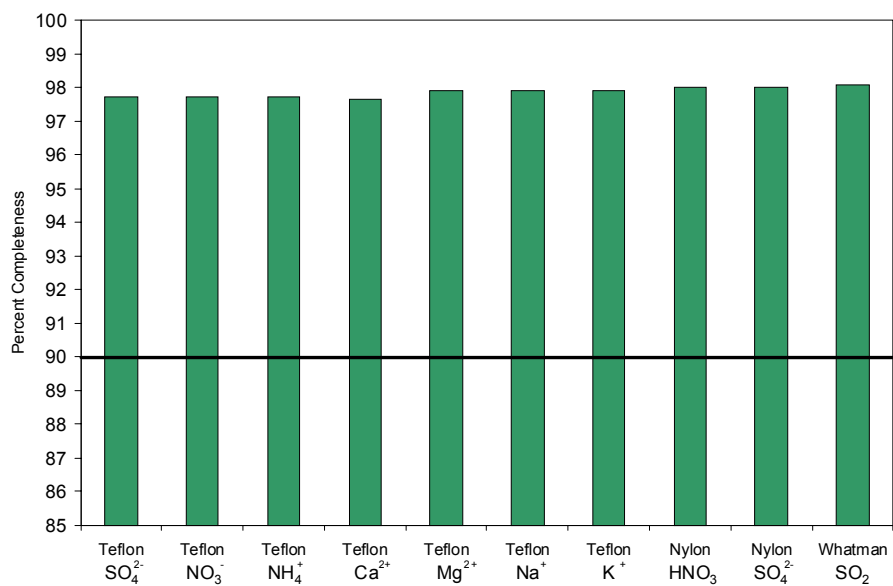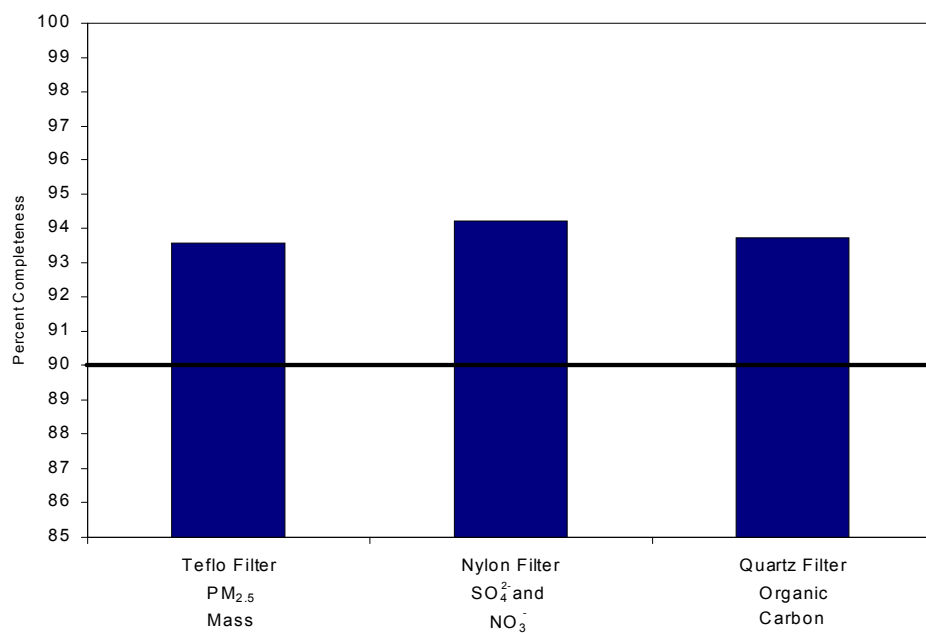
Figure 6-8. Percent Completeness of Continuous Measurements for 2000

Figure 6-9. Percent Completeness of Concentration Measurements by Filter Type for 2000

Figure 6-10. Percent Completeness of Concentrations Measured on Aerosol (Visibility) Filters for 2000

Figure 6-11. Percent Completeness of Hourly Dry Flux Estimates for 2000